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A SEARCH FOR PRESOLAR ORGANIC MATTER IN METEORITE

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Abstract. The D/H ratios and the $^{13}C/^{12}C$ ratios of acid-insoluble organic matter of 4 meteorites, Ochansk (H4), Plainview (H5), Gladstone (H6) and Odessa (IA), were measured. δD values for hydrogen extracted by stepwise combustion were negative, down to -280°/₀₀. $\delta^{13}C$ values were also negative except in the case of the carbon coming off at the highest temperature steps for Plainview and Odessa meteorites. The concentrations of ^{13}C-rich carbon were 3-5 orders of magnitude smaller than those found in Murchison meteorite, suggesting that relic grains of stellar condensates were mostly destroyed in the meteorites examined.

Introduction

Hydrogen isotope studies of acid residues from various meteorites suggested that organic matter of high D/H ratio is probably originated from interstellar organic molecules and is present in large quantities in some of the unmetamorphosed meteorites [Smith and Rigby, 1981; Robert and Epstein, 1982; Yang and Epstein, 1983a]. δD values of such organic matter were above 1,000°/₀₀ in most cases and up to about 10,000°/₀₀ in some cases. Types 4-6 ordinary chondrites and differentiated meteorites [Yang and Epstein, 1983a] contained organic matter whose δD values were similar to terrestrial hydrogen, between -200°/₀₀ and 200°/₀₀, except Kelly (LL4) whose δD value was 380°/₀₀. $\delta^{13}C$ values of the organic matter had a much narrower range of -31°/₀₀ and -12°/₀₀ [Briggs, 1963; Smith and Kaplan, 1970; Robert and Epstein, 1982; Swart et al., 1982; Yang and Epstein, 1982, 1983a]. The $\delta^{13}C$ variation of about 20°/₀₀ in carbon samples of metamorphosed meteorites is probably an indication of isotopic fractionation processes due to a loss of carbon during metamorphism [Yang and Epstein, 1983a]. When Murchison meteorite (CM2: carbonaceous chondrite of petrologic type 2) samples which were treated with HCl-HF and with various oxidizing chemicals were combusted by stepwise heating, the CO_2 gas extracted at temperatures above 800°C gave $\delta^{13}C$ values up to 1500°/₀₀ [Kerridge, 1983; Swart et al., 1983; Yang and Epstein, 1983b, 1984]. Swart et al. [1983] considered that this ^{13}C-rich carbon was originated from red giant star materials. Assuming that all types of meteorite were originally made up of similar material, the degree of elimination of the D-rich hydrogen and the ^{13}C-rich carbon should be an indication of the degree of metamorphism for petrologic types 4-6 ordinary chondrites and differentiation for iron meteorite.

Experimental Procedures

In this study we used three bronzite chrondrites (H) and an iron meteorite of group IA — Ochansk (H4), Plainview (H5), Gladstone (H6) and Odessa (IA). Whole rock meteorite samples were treated with various chemical reagents following the procedure described by Yang and Epstein [1983b, 1984] and Alaerts et al. [1979].

Two sets of samples were prepared. The first set of samples, labeled CFO, are the bulk meteorites which were treated successively by 10M HCl, 9M HF-1M HCl, 70% $HClO_4$, 90% fuming HNO_3, 30% H_2O_2 and 3M NaOH-0.4M NaOCl (all at 100°C except HF-HCl which was at 23°C), and were washed in distilled water and then in acetone. The yields of the residues ranged between 0.37 and 1.03% (Table 1). A terrestrial shale sample was also treated in a similar manner to assure that any isotopic fractionations due to our procedures would be revealed in this way.

The second set of samples, labeled CFOP, are the CFO samples which were treated further with boiling 70% $HClO_4$ to remove organic hydrogen and to concentrate heavy carbon by removing organic carbon with low $\delta^{13}C$ values (see Yang and Epstein, 1984 for more details of chemical effects). The resulting yields by weight ranged between 0.0053 and 0.32% (Table 1). We obtained 10 acid residue samples from 4 meteorites and a shale. Odessa iron meteorite contains large black spherical inclusions. We separated out some of these inclusions during the early stage of chemical treatments for separate analyses.

Gases (H_2, CO_2, SO_2, N_2) were extracted in a quartz vacuum system which was designed to minimize the blank of the system. Samples were wrapped with Pt foil and all samples were loaded at the same time. The main system consists of several fingers for copper oxide (provides oxygen), uranium (converts H_2O to H_2 gas), cold liquids (separates gases), Pd-Ag (passes H_2 gas) and a resistant heater (heats samples stepwisely with ±5°C accuracy). Gases (N_2, CO_2, SO_2) were collected by a Toepler pump which is connected to the main quartz system by a metal bellow valve which is the only valve in the system. Every part of the system was heated thoroughly above ~600°C before every sample run.

TABLE 1. The data of total concentrations of carbon and the ratios of H/C, N/C and S/C in the two kinds of acid residues of H4-6 & IA meteorites and shale.

Sample	weight %	C μmoles/g[a]	H/C	N/C	S/C
CFO [HCl, HF, H_2O_2, HNO_3, NaOH-NaOCl]					
OCHANSK(H4)	1.03	36.7	0.069	~0.009	~0.008
PLAINVIEW(H5)	0.84	11.7	0.038	~0.02	~0.0009
GLADSTONE(H6)	1.02	13.9	0.21	~0.03	~0.1
ODESSA(IA)	0.37	247	0.008	~0.002	~0.0002
Shale	2.07	718	0.28	0.039	0.0068
CFOP [HCl, HF, H_2O_2, HNO_3, NaOH-NaOCl, $HClO_4$]					
OCHANSK	0.010	0.066	~0.9	~0.9	<0.03
PLAINVIEW	0.0069	0.041	~0.6	~0.1	~0.02
GLADSTONE	0.0053	0.018	~3	<1	<0.1
ODESSA	0.32	241	0.009	<0.0004	~0.00007
Shale	0.21	4.5	~0.7	~0.09	0.004
ODESSA inclusion	≥0.37	~205	0.0008	~0.00008	0.022

[a]The concentration is given in μmoles per gram of bulk samples of meteorites and terrestrial shale.

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TABLE 2. The concentrations and the isotopic data of H and C released by stepwise oxidation - pyrolysis of acid residues of four meteorites and a terrestrial shale.

Sample	T[a] °C	H_2 μmoles/g[b]	δD	CO_2 μmoles/g[b]	$\delta^{13}C$	C/H
CFO RESIDUES						
OCH	(350)	2.91	-10	0.59	-25.7	0.10
167 mg	700	0.85	-76	32.7	-25.6	19
	800	0.29	-148	3.1	-25.3	5.3
	900	~0.04	~-190	0.12	-34.7	~2
	1100	~0.08	~-217	0.21	-22.2	~1
	Total	1.26	-105	36.7	-25.6	15
PLA	(350)	0.62	-50	0.18	-22.5	0.15
191 mg	800	0.18	-56	11.5	-17.3	32
	900	~0.02	~-196	0.044	~-55	~1
	1100	~0.02	~-177	~0.003	~50	~0.1
	Total	0.22	-80	11.7	-17.5	27
GLA	(350)	4.56	-9	0.35	-28.8	0.038
132 mg	800	1.32	-68	13.1	-22.9	5.0
	900	~0.09	-206	0.17	-8.8	~0.9
	1100	~0.05	~-280	0.31	-25.1	~3
	Total	1.46	-84	13.9	-22.9	4.8
ODE	(350)	1.09	-59	1.1	-24.4	0.50
22.4 mg	700	0.63	-106	45	-6.2	36
	800	0.28	-68	201	-4.7	360
	900	~0.02	~-62	~0.026	~-31	~0.7
	1100	~0.07	~-39	~0.012	~31	~0.1
	Total	1.00	-90	247	-5.1	120
Shale	(350)	89	-33	80	-31.5	0.45
15.8 mg	700	80	-105	153	-28.1	0.96
	800	22	39	485	-26.9	11
	900	<0.5	—	0.19	-27.3	—
	1100	<0.5	—	0.71	-25.4	—
	Total	102	-74	718	-27.7	3.5
CFOP RESIDUES						
OCH	(350)	~0.04	~-36	0.039	-25.2	~0.5
1.8 mg	800	~0.01	~-42	0.017		~0.9
	1100	~0.02	~-43	~0.01	~-13	—
	Total	~0.03	~-43	0.066	~-23	~1.1
PLA	(350)	~0.02	~-81	0.002	-17.0	~0.05
2.8 mg	800	~0.007	~-151	0.038		~2.7
	1100	~0.005	~-141	~0.001	~26	—
	Total	~0.012	~-147	0.041	~-16	~1.7
GLA	(350)	~0.047	~-49	0.003	-24.1	~0.03
1.0 mg	800	~0.02	~-117	0.012		~0.3
	1100	~0.01	~-110	~0.003	~-31	~0.2
	Total	~0.03	~-115	0.018	~-25	~0.3
ODE	(350)	0.41	10	0.28	-19.3	0.34
15.3 mg	900	1.88	-18	241	-5.3	64.1
	1100	~0.24	~16	0.021	~31	0.044
	Total	~2.12	~-14	241	-5.3	~57
ODE	(350)	0.58	~-17	0.48	-19.5	0.41
173 mg	700	0.61	~-5	55	-5.4	45
	800	0.20	-216	42	-5.0	105
	900	0.18	-160	18	-5.3	51
	900	0.12	-209	120	-4.8	480
	900	<0.02	—	2.6	-4.7	>65
	1000	<0.01	—	0.015	~19	>0.7
	1100	<0.01	—	0.031	~12	>1.5
	Total	1.11	-90	238	-5.0	110
Shale	(350)	0.98	34	0.21	-23.0	0.11
2.5 mg	800	1.22	-23	3.98		1.63
	1100	~0.3	~-58	0.30	-17.6	~0.5
	Total	~1.5	~-30	4.5	-22.6	~1.5
INCLUSION						
ODE	(350)	~0.19	132	~0.008	-5.0	0.021
140.2 mg	800	~0.054	56	~10.9		101
	900	~0.02	~-107	~193	-4.9	4830
	900	~0.003	—	~1.26	-5.2	210
	1100	~0.004	~-200	~0.004	~-9.7	~0.5
	Total	~0.078	~1	~205	-4.9	1300

[a]T in parentheses represents the heating step without oxygen. Samples were heated for 1-3 hours at each heating step except underlined steps where samples were heated for 4-16 hours.
[b]Yields are given in μmoles per gram of bulk samples.

Incidentally this was the identical system used with the study of Murchison samples. The blanks were especially low in carbon, nitrogen and sulfur, ~0.03 μmoles each. Hydrogen and carbon gas samples were analyzed by standard stable isotope ratio mass spectrometers and reported in usual δ notations. δ is the deviation in isotopic ratios with respect to standards in parts per thousand (‰). The standards for hydrogen and carbon are standard mean ocean water and PDB, respectively.

Results and Discussion

Table 1 shows the percentage yield of the CFO and CFOP residues and the concentration of carbon in the residues. For the three H chordrite samples boiling the CFO residues with 70% $HClO_4$ resulted in a loss of more than 99.6% of the total carbon and more than 99% of the total weight. The perchloric acid, therefore, removed most of the material (chromite, spinel and carbon) and left a small amount of very oxidation-resistant material. Table 1 also shows the hydrogen, nitrogen and sulfur concentrations in the samples relative to carbon for comparison. A very small amount of the nitrogen and sulfur remained in the residues after treatment, ≤1 μmole/g for CFO and <0.1 μmole/g for CFOP, so that isotopic measurements were not made for these gases. Carbon contents in Odessa meteorite samples are somewhat surprising. The weight percentages of carbon in the two residues are 81% (CFO) and 90% (CFOP). Virtually no carbon in CFO Odessa sample was lost by perchloric acid treatment.

Table 2 shows the isotopic data and the concentrations of hydrogen and carbon released by stepwise combustion of the acid residue samples. Note that the first heating step, 350°C, was straight pyrolysis in absence of oxygen gas. Under this condition, we

found that terrestrial hydrogen could be degassed but the indigenous organic hydrogen of the samples is more stable in absence of O_2 and comes off at above 350°C. We consider the 350°C fraction of hydrogen as of terrestrial origin.

δD values for the total hydrogen of meteorites are -105°/₀₀ to -79°/₀₀ for CFO samples and -147°/₀₀ to -14°/₀₀ for CFOP samples. The ranges of δD values of hydrogen from stepwise heating are -280°/₀₀ to -39°/₀₀ for CFO samples and -216°/₀₀ to -5°/₀₀ for CFOP samples. These δD values are quite similar to the δD values of HCl-HF residues from metamorphosed and differentiated meteorite samples studied in Yang and Epstein [1983a]. The δD values and the concentrations of hydrogen per gram of CFO acid residue samples, 26–270 μmoles/g, fit well in the plot of δD vs. hydrogen concentrations in Yang and Epstein [1983a]. However, the concentrations of the hydrogen are very low and the δD values of this hydrogen and the δD of the inorganic meteorite hydrogen (-110°/₀₀) are similiar [Yang and Epstein, 1983a]. These results might suggest that the high temperature history of these meteorites allow the direct or indirect equilibration of the hydrogen in the organic matter with the inorganic hydrogen formed in the beginning of the solar system formation [Yang and Epstein, 1983a].

The range of $\delta^{13}C$ values of total carbon in the CFO and CFOP samples of H chondrites is between -26°/₀₀ and -16°/₀₀. If the different carbons given out at different temperatures are considered, this range expands to between -55°/₀₀ and +50°/₀₀. The $\delta^{13}C$ value of total carbon for CFO and CFOP samples of Odessa iron meteorite is -5°/₀₀. The range of $\delta^{13}C$ values of carbon from all temperature steps is between -31°/₀₀ and +31°/₀₀. $\delta^{13}C$ values of the carbon released at different temperatures for a given sample are often constant if we exclude carbons from the lowest and the highest temperature steps. This is best shown in Odessa CFOP sample and demonstrates that the gas extraction procedure effectively separated different carbon components. A terrestrial shale sample was chemically treated the same way as the meteorites. The gas analyses of the residues CFO and CFOP showed no unusual isotopic values for both δD and $\delta^{13}C$, indicating that the chemistry applied to the meteorites and the gas extraction procedure do not significantly change the isotopic values of the meteorites by isotopic fractionations from chemical and distillation processes.

While the carbon samples of Ochansk and Gladstone meteorites all gave $\delta^{13}C$ less than -8°/₀₀, carbon of Plainview and Odessa meteorites released at temperatures above 900°C gave $\delta^{13}C$ values of 12 to 50°/₀₀. These positive $\delta^{13}C$ values are not as large as those found in high temperature release carbon of Murchison acid residues. However, it is quite possible that they originated from the same source because the sample preparations were almost identical. Also, the residues consist of similar material (chromite, spinel and organic polymer) and the isotopic patterns from stepwise combustion are the same.

The C/H ratios (Table 2) of CFO residues of three H chordrites are 4.8 to 27. CFO and CFOP samples of Odessa iron meteorite showed unusually high C/H ratios of 110 to 120. Perhaps the carbon in this Odessa meteorite was formed by decomposition of organic matter during differentiation process unlike the other three meteorites. The existence of the high positive $\delta^{13}C$ values in Odessa meteorite may possibly give information about the thermal history of the parent-body from which Odessa originated by the degree of homogenization of the total carbon and hydrogen.

We may compare the concentrations of the ^{13}C-rich carbon of the Murchison residues with those of the 4 meteorites we studied here. If the concentrations of the carbon with positive $\delta^{13}C$ values are compared, Murchison residues contain 0.1 to 4.0 μmoles per gram of bulk meteorite sample and the residues of Plainview and Odessa contain 0.001 to 0.046 μmoles per gram of bulk meteorite sample. Therefore, Murchison contains about two orders of magnitude more carbon of positive $\delta^{13}C$. It may be more appropriate, however, to compare the concentrations of heavy carbon by assuming the same $\delta^{13}C$ value. Previously we have used the maximum $\delta^{13}C$ value observed, 1500°/₀₀, as a heavy carbon component [Yang and Epstein, 1983b]. Assuming there are two carbon components, a low $\delta^{13}C$ value of -30°/₀₀ and a high $\delta^{13}C$ value of +1500°/₀₀, the Murchison samples contained 1.3 to 66 ppm of 1500°/₀₀ $\delta^{13}C$ carbon component. Similarly, we could calculate the concentrations of such a ^{13}C-rich carbon component in Plainview and Odessa residues. They contain 0.3 to 2 and 4 to 6 ppb of 1500°/₀₀ $\delta^{13}C$ carbon component (Table 3). Therefore, the two meteorites contain 3 to 5 orders of magnitude less heavy carbon compared to Murchison meteorite.

Metamorphism temperature for H4-6 chondrites is estimated to be about 600-830°C [Dodd, 1981; Lingner, Huston, and Lipschutz, 1984; Olsen and Bunch, 1984].

TABLE 3. The δD values and the concentrations of carbon of 1500°/₀₀ $\delta^{13}C$ in acid residue samples of meteorites.

Sample	δD[d] °/₀₀	heavy carbon ppm	Ref.
MURCHISON, CM2			
H_3PO_4		2.2	a
2C10f		3.5	a
2C10m		0.6	a
CF	607	30	b
CFOc	2560	8.6	b
CFOf	952	37	b
CFOfN	301	2.8	b
CFP	214	1.3	b
P	-86	2.6	b
PCF	—	1.3	b
CFS	772	66	b
ALLENDE, CV3			
BB		0.7	a
BG		0.5	a
B1B		—	a
OCHANSK, H4			
CFO	-105	—	c
CFOP	-43	<0.004	c
PLAINVIEW, H5			
CFO	-80	~0.002	c
CFOP	-147	~0.0003	c
GLADSTONE, H6			
CFO	-84	—	c
CFOP	-115	<0.0007	c
ODESSA, IA			
CFO	-90	~0.004	c
CFOP	-90	~0.006	c

[a]Swart et al. [1983].
[b]Yang and Epstein [1983b, 1984].
[c]This work.
[d]The hydrogen released at 350°C pyrolysis is not included in the summation of the total hydrogen for this δD.

The cooling rates of type 4-6 ordinary chondrites and iron meteorite at above ~600°C are much higher than those at lower temperatures [Pellas and Storzer, 1981; Taylor and Scott, 1984]. Therefore, it may be possible that a major thermal isotopic effect occurred during cooling at, say, 600°C to 500°C. The duration of that cooling period is about <2 to 14 myr for H4-6 [Pellas and Storzer, 1981] and 0.25 to 22 myr for iron meteorites [Pellas and Storzer, 1981; Narayan and Goldstein, 1983].

Perhaps the thermal history of about 600°C for an order of 1 myr of the 4 meteorites we studied here was severe enough to destroy the anomalous D and ^{13}C isotopic values of hydrogen and carbon by homogenization. The difference in $\delta^{13}C$ values of total carbon between Odessa and the other three H chondrites is about 20‰ and such a value could be interpreted as a consequence of a thermal isotopic fractionation. However, the thermal history was mild enough or the mechanisms involved in homogenization slow enough for some meteorites such as Plainview and Odessa to preserve some heavy carbon even though the amount is small. All meteorites but Ochansk are finds. However, this fact does not relate with any of the trend we observed. More quantitative and meaningful constraints could be made when we understand the physical and chemical environment of the meteorite parent body more accurately.

Conclusions

Table 3 summarizes the δD values and the concentrations of the heavy carbon of 1500‰ $\delta^{13}C$ found in the acid residues of meteorites studied so far. Clearly CFO and CFOP samples lack the deuterium-rich organic matter formed in the interstellar medium. The concentrations of the ^{13}C-rich carbon in these samples are 3-5 orders of magnitude lower than acid residues of two carbonaceous chondrites, Murchison (CM2) and Allende (CV3). Such deficiencies could be due to the metamorphism for H4-6 and the differentiation processes for iron meteorites. Indigenous isotopic patterns could be erased during such high temperature episodes by isotopic homogenization between ^{13}C-rich carbon and normal carbon in organic matter and carbonates.

The absence of high δD and the small enrichments in the $\delta^{13}C$ suggest the loss of hydrogen and carbon and the homogenization of the remaining fraction of these elements during metamorphism. The small residual $\delta^{13}C$ enrichment may or may not be indicative of survival of originally high $\delta^{13}C$ carbon (~1500‰) and thus these meteorites may have been void of ^{13}C-rich carbon prior to metamorphism. More detailed analyses of the residues may contribute to the answer to this alternative.

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